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(54) IMPROVEMENTS IN OR RELATING TO METHODS OF  
 GASIFYING HYDROCARBONS

(71) We, BRITISH GAS CORPORATION, (formerly The Gas Council), a British Body Corporate, of 59 Bryanston Street, Marble Arch, London, W1A 2AZ., do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method of performing a reforming reaction in the presence of steam and hydrogen, in such a manner that the effective life of the catalyst employed in the reaction is prolonged.

Reforming reactions which are effected in the presence of steam and hydrogen are well known. It is to be understood that the term "hydrogasification" as used herein refers to the steam reforming of vaporisable hydrocarbon feedstocks in the presence of hydrogen.

British Patent Specification No. 1,053,855 describes and claims a particular reforming reaction which is carried out in the presence of steam and hydrogen, and is particularly concerned with a process for the manufacture of a methane-containing gas which process comprises passing a heated mixture of a hydrocarbon feedstock which is liquid at normal temperatures and pressures, and boils below 300°C., from 0.1 to 2.5 lb. moles of hydrogen and at least 0.3 lb. moles of steam per pound atom of carbon in the feedstock, the mixture having a sulphur content of not more than 0.025 grains per 100 standard cu.ft. through a bed of highly active particulate solid metal catalyst under such conditions that the mixture reacts to produce substantially only products which are gaseous at standard temperature and pressure.

British Patent Specification No. 1,265,481 also describes and claims a particular reforming reaction which is carried out in the presence of steam and hydrogen, and is particularly concerned with a process which comprises (i) introducing a preheated mixture of steam and the vapour of a pre-

dominantly paraffinic hydrocarbon feedstock having a final boiling point of not more than 300°C. into a first catalytic reaction zone in which the mixture reacts in the presence of a steam reforming catalyst, to give a gas containing methane, hydrogen, carbon oxides and undecomposed steam; (ii) cooling the gas produced in stage (i) by adding a further quantity of at least one of the reactants; (iii) introducing the gaseous mixture formed in stage (ii) into a second catalytic reaction zone in which the constituents of the mixture react in the presence of a catalyst to increase the proportion of methane in the mixture; and (iv) removing steam from the gas leaving the second catalytic reaction zone, to produce a gas containing at least 85% by volume of methane on a dry carbon and dioxide free basis.

It is known that some catalysts which are suitable for use in reforming reactions carried out in the presence of steam and hydrogen, such as coprecipitated nickel-alumina compositions containing a small proportion of alkali or alkaline earth metal compounds suffer gradual loss of activity as a result mainly of the formation of submicroscopic layers of material derived from the feedstock on the surface. The disadvantages resulting from this phenomena have been overcome to the extent that steam reforming processes which are carried out in the presence of hydrogen are well established, and adequate catalyst lives have been achieved.

It is, however, desirable to increase still further the life which can be obtained in practical operations from a given quantity of catalyst, and we have now surprisingly discovered a process which permits the prolongation of the effective life of such catalyst.

The present invention is based upon the discovery that when catalyst has been deactivated by the formation on its surface of sub-microscopic deposits derived from hydrocarbon feedstock, the activity of the

catalyst can be restored, at least partially, by exposing the catalyst to hydrogen or to a hydrogen containing gas, the said exposure being carried out at or near a normal working temperature for the catalyst, preferably for a substantial period of time. It is possible that steam also contributes to the regeneration.

Accordingly, in order to improve the use of a quantity of catalyst in a reforming reaction which is carried out in the presence of steam and hydrogen, the present invention provides a method of performing a reforming reaction which method comprises reacting a vaporisable hydrocarbon feedstock, steam and hydrogen in the presence of a reforming catalyst of the type which, in use, suffers from inactivation as a result of the formation thereon of sub-microscopic layers of material from constituents of the feedstock, the said method employing the improvement which comprise (1) passing the reactants through a first bed of catalyst to effect the steam reforming reaction until the activity of the first bed of catalyst has substantially deteriorated, (2) then switching the stream of reactants to a second bed of catalyst to effect the steam reforming reaction in said second bed until the activity of the second bed of catalyst has substantially deteriorated, a hydrogen containing gas being passed through the first bed to regenerate catalytic activity in the said first bed, and (3) then switching the stream of reactants to the regenerated first catalyst bed and continuing the steam reforming reaction in the said regenerated first catalyst bed.

It will be understood by those skilled in the art that the removal of polymer is not attempted under conditions whereby further polymer would be formed. Generally therefore the regeneration step will be carried out in the substantial absence of vaporisable hydrocarbon feedstock.

The second stage of the method of the invention may be carried out using the second bed of catalyst and the first bed of catalyst in series. Preferably in putting into practice the method of the invention, as the activity of the second bed of catalyst deteriorates the incompletely reacted reactants and the product gas are passed from the second bed to the regenerated first bed of catalyst where the steam reforming reaction is completed.

The hydrogen containing gases used in the catalyst regeneration of the first catalyst bed may be, for example, the gases produced in the hydrogasification reaction carried out in the second catalyst bed, or gasification gases produced by the steam reforming of vaporisable hydrocarbon feedstocks, or a mixture of such gases. A particular steam reforming process which is

described in British Patent Specification No. 820,257, has become known as the C.R.G. (Catalytic Rich Gas) process. Other examples of hydrogen containing gases which may be used are pure hydrogen, hydrogen-nitrogen mixtures or "lean gas", that is, high temperature reformer gas, rich in hydrogen, after any suitable degree of carbon dioxide removal and carbon monoxide conversion.

When either hydrogasification gas, or more particularly catalytic rich gas, is used in the regeneration step, methane synthesis from carbon oxides and hydrogen may take place on the catalyst which is undergoing regeneration, without in any way impairing the effectiveness of the regeneration. Thus, a hydrogasification catalyst which, in use, is inactivated by the formation of sub-microscopic layers of polymeric material thereon, may be regenerated by using it as a methane synthesis catalyst.

Accordingly in one particular aspect the present invention provides a method of performing a reforming reaction, wherein the regeneration of the catalytic activity of the first bed of catalyst is effected by the passage through the said bed of hydrogasification gas, catalytic rich gas or a mixture thereof, under conditions whereby methane synthesis is effected.

The sub-microscopic layer of material derived from constituents of the feedstock which deactivates the catalyst is believed to be a polymeric material of unknown molecular weight which commonly has an atomic hydrogen/carbon ratio of less than 2; it is likely to be principally an assembly of condensed aromatic rings. Such material has often been referred to as "polymer". It is preferred in accordance with the present invention to employ catalysts comprising nickel, preferably supported on a refractory oxide, such as alumina.

The catalysts may be co-precipitated nickel-alumina catalysts containing an addition of an oxide, hydroxide or carbonate of an alkali metal or alkaline earth metal, such as are described in our British Patent Specification No. 969,637. The proportion of the added alkali metal or alkaline earth metal compound if preferably from 0.75% to 8.6% calculated as metal based on the combined weight of the nickel and alumina. A particularly preferred catalyst is one containing from 70 to 75% nickel, 0.8% potassium and the balance being alumina. An alternative preferred catalyst is a co-precipitated nickel-alumina catalyst containing at least 40% nickel and from 0.10% to 0.75% of an alkali metal in the form of an oxide, hydroxide or carbonate, percentages being by weight of the metal based on the combined weights of the nickel and alumina, such as are described in our British

Patent Specification No. 1,150,066. A particularly preferred catalyst of the latter type is one containing from 70 to 75% nickel, 0.2% potassium and the balance being alumina. While the operations described are beneficial to a greater or lesser degree to the operation of all catalysts that suffer regeneratable deactivation, they are likely, with catalysts according to the above specifications, to be more beneficial with those containing the lower proportions of alkali, since these are more sensitive to deactivation by "polymer" and are believed to be less liable to sinter, than catalysts containing significantly higher proportions of alkali. Thus for example, the use of catalysts prepared according to our British Patent Specifications Nos. 1,155,843 and 1,158,786, containing at least 10% by weight of alkaline earth metal, may benefit less from the procedure described than when catalysts prepared according to our Specifications Nos. 969,637 and 1,150,066 are used, but nevertheless operation with them according to this procedure falls within the scope of the invention. The catalyst may be present in the form of a fluidized bed which is maintained in this condition by the passage of reactants through the bed. Alternatively, the catalyst may be present in the form of a fluidized bed which is maintained in this condition by the passage of reactants through the bed. Alternatively, the catalyst may be in pellet form in the normal type of fixed bed.

It will be appreciated that the lower the temperature at which the deactivating "polymer" is formed and deposited, the easier it is to remove with hydrogen. The "polymer" however tends to be formed more readily at lower temperatures, and the inlet temperature to the hydrogasification stage is therefore a compromise temperature, for example 350°C to 450°C.

Regeneration, whether using catalytic rich gas or hydrogasification gas (or pure hydrogen) can be carried out within the temperature range 300 to 550°C, the choice of temperature being influenced by the question of how far sintering of the catalyst is liable to occur and by the extent to which it is necessary to minimise it. Preferably, regeneration is effected by preheating the regenerating gas to a temperature not less than that at which the reactants are supplied when hydrogasification is in progress.

The hydrogasification steps of the process of the invention may be carried out according to the method described in British Patent Specification No. 1,053,855. Thus, a heated mixture of a vaporisable hydrocarbon feedstock, from 0.1 to 2.5 lb. moles of hydrogen and at least 0.3 lb moles of steam per pound atom of carbon in the feedstock may be passed through a bed of catalyst under conditions such that the mix-

ture reacts to produce substantially only products which are gaseous at standard temperature and pressure. The hydrogen may be supplied as hydrogenating gas, for example, catalytic rich gas.

The hydrogasification steps of the process of the invention may also be carried out according to the particular method described in British Patent Specification No. 1,265,481.

In another mode of operating the process of the present invention one or more of the hydrogasification stages of the process may be effected by recycling a portion of the product gases produced in the reforming reaction and mixing these gases with the hydrocarbons and steam to be reacted prior to the passage of the mixture through the bed of catalyst. The recirculation of the gases may be effected using a fan, a compressor, a turbo-blower or a jet pump. The jet pump may be driven by steam, hydrocarbon feedstock vapour or a mixture of both and is preferably one which comprises a section of decreasing cross-sectional area connected by its narrower end to a substantially cylindrical mixing throat, there being disposed centrally in the section of decreasing cross-sectional area a jet, for example a jet for the provision of high pressure steam, which jet terminates just before the mixing throat, means for the introduction of recycled gases being provided in the section of decreasing cross-sectional area.

Various arrangements and operational procedures, which do not exhaust all the possibilities, can now be described by way of examples. They will be best understood by reference to the accompanying process line diagrams.

#### EXAMPLE I

Referring to Figure 1, vessel No. 1. is operational as a hydrogasifier and will accept all the naphtha feedstock and steam via A and the bulk of the catalytic rich gas via C. A small stream of catalytic rich gas passes through the small bypass valve D' for the regeneration of the catalyst in vessel No. 2. The commingled streams from 1 and 2 together constitute the product gas. It is known that for constant preheat (the arrangements for which are not shown) the gases issuing from 1 and 2 are of substantially the same composition so that the composition of the mixture is affected little if at all by the proportions in which the catalytic rich gas is divided.

In order to operate in the manner stated, valves A, C, D' are opened and valves B, C' and D are closed.

Regeneration of the catalyst in vessel 1 and hydrogasification using the regenerated catalyst in vessel 2 is achieved by reversal of the valves, at the end of which operation

valves B, C' and D are open, and valves A, C and D' are closed.

#### EXAMPLE II

Referring to Figure II, the vessel arrangement shown allows for the regeneration of a hydrogasification catalyst using the product gases from another hydrogasifier. When vessel No. 1. is operating as a hydrogasifier and vessel No. 2 is being regenerated, valves B, A, H, K and F are open and valves C, D, G, E and J are closed.

Regeneration of the catalyst in vessel No. 1 and hydrogasification using the regenerated catalyst in vessel No. 2. is achieved by appropriate reversal of certain valves at the end of which operation C, D, E, K, H and G are open and valves B, A, F and J are closed. It will be seen that with pipework arranged in the usual sense represented by the drawings gasification and regeneration take place in opposite directions in the vessels.

The apparatus shown may however be used for regeneration by catalytic rich gas as before, if this is desired, by the use of the valves B', D' and J. With operation of vessel No. 1, as a hydrogasifier, the product gas flowing to the outlet via H and J, a bleed of catalytic rich gas for regeneration can be admitted to vessel No. 2 via D' and the process can be reversed.

Valves H and K in Figure II are provided for isolation purposes if necessary, with operation on the working vessel via J. Similar provision could clearly be made in the apparatus of figure I if desired.

#### EXAMPLE III

Referring to Figure III, the vessel arrangement shown closely resembles that described in Example II, the principal difference being that provision is made for flow of regenerating hydrogasification gas (as well as catalytic rich gas, where used) to be in the same direction through the catalyst bed as the flow of reactants where hydrogasification is in process.

When vessel No. 1 is operating as a hydrogasifier and vessel No. 2 is being regenerated, valves C, A, G, F and J are open and B, D, E, H and K are shut. When the functions of the vessels are reversed, valves B, D, H, E and K are open and valves A, C, F, G and J are closed.

The by-pass or "bleed" valves C', D', will permit the regeneration of one vessel with catalytic rich gas while the other is operational. For instance, with vessel No. 2 acting as the hydrogasifier, and vessel No. 1 being regenerated with catalytic rich gas admitted via C', the two streams flow to the product gas outlet via J and K respectively, G and H being closed.

The by-pass or "bleed" valves E', F',

can similarly be used for regeneration with hydrogasification gas, or with the catalyst in one vessel being in parallel with operation of hydrogasification in the other. Thus, with vessel No. 1. operational as a hydrogasifier, the larger stream of product gas passing to the outlet via K, regeneration of the catalyst in vessel No. 2 can be achieved with the lesser stream of product gas flowing through G, F' and J, while H is closed.

#### EXAMPLE IV

Referring to Figure IV, 1 and 2 are vessels containing catalyst which are arranged so that the regeneration of a hydrogasification catalyst in one vessel may be effected using the product gases from the other vessel.

In the particular vessel arrangement illustrated hydrogasification is carried out in vessel 1. A portion of the product gases issuing from vessel 1 via valve G is recirculated to vessel 1, thereby providing the hydrogen-containing gas for the hydrogasification reaction. The recirculated product gas is mixed in the fresh steam and naphtha and raised in pressure by a fan X and enter vessel 1 through valves A and C, valves B and D being closed. It will be understood that it will generally be preferable to introduce the fresh steam and naphtha downstream of fan X, rather than upstream, as is shown in the Figure. The products of gasification leave vessel 1 via valve G and the recirculated stream returns to the fan X. The unrecirculated stream flows through valve H to vessel 2 where regeneration of a catalyst whose activity has been affected in an earlier phase of operation takes place. The unrecirculated stream may undergo methanation and leaves vessel 2 via valves F and E.

In the alternate phase, the hydrogasification will proceed in vessel 2, around which there will be recirculation, whilst the catalyst in vessel 1 will be regenerated. The flow paths are not shown with arrows. Valves B, F and H are open to provide the recirculation path, valves A and E being shut, and the unrecirculated stream flows through vessel 1 and out of the system via valves G, C and D. It will be apparent that certain pipes are used in different directions in the different phases of operation, so that the arrows shown on the Figure are not intended to apply to the second phase as described.

Whilst this particular example has been described using a fan X to provide recirculation of a portion of the product gases issuing from the hydrogasifier it will be appreciated that recirculation may be provided by any means, for example the fan may be replaced by a compressor, a turbo-blower or a jet pump. When the latter device is used

it is preferable to use the fresh process steam, optionally together with the fresh hydrocarbon vapour, as the driving fluid in the pump, to entrain the mixture being recirculated from the outlet of the gasification reactor.

Other arrangements of vessels and pipe-work which allow the catalyst in one reactor to be employed for hydrogasification and that in the other to be undergoing regeneration, either in series, with hydrogasification product gas, or in parallel, either with catalytic rich gas or hydrogasification product gas, can be devised and are within the scope of the invention. Such arrangements comprise those where it is desired that regeneration gas shall enter at the same end of the vessel as do the reactants when the vessel is operational, and those where the flow in the two phases of operation is in opposite directions.

If regeneration is carried out with hydrogasification gas, it may be desired to ensure that methanation takes place on the catalyst undergoing regeneration. In general, achieving this is simply a matter of ensuring correct temperature adjustment of the gas as it flows along the pipe connecting the operating hydrogasifier with the vessel undergoing regeneration. For instance, a heat exchanger may be interposed between valves H and K in Figure II, so as to reduce the temperature of the mixture leaving hydrogasifier No. 1 and 2, as the case may be, to a value appropriate to ensure methane synthesis taking place when the mixture enters hydrogasifier No. 2 or No. 1 to perform regeneration.

Similar provision of temperature adjustment for the control of methanation taking place during regeneration with catalytic rich gas may be made. It is, indeed, to be understood that any desirable heating or cooling of reactants or gas streams, by conventional means, at points not shown in the drawings, may be applied to control the reactions occurring in the various catalyst vessels.

#### WHAT WE CLAIM IS:—

1. A method of performing a reforming reaction which method comprises reacting a vaporisable hydrocarbon feedstock, steam and hydrogen in the presence of a reforming catalyst of the type which, in use, suffers from inactivation as a result of the formation thereon of sub-microscopic layers of material from constituents of the feedstock, the said method employing the improvement which comprises (1) passing the reactants through a first bed of catalyst to effect the steam reforming reaction until the activity of the first bed of catalyst has substantially deteriorated, (2) then switching the stream of reactants to a second bed of catalyst to effect the steam reforming re-

action in said second bed until the activity of the second bed of catalyst has substantially deteriorated, a hydrogen containing gas being passed through the first bed to regenerate catalytic activity in the said first bed, and (3) then switching the stream of reactants to the regenerated first catalyst bed and continuing the steam reforming reaction in the said regenerated first catalyst bed.

2. A method as claimed in claim 1 wherein the hydrogen containing gases used in the regeneration of the first catalyst bed are hydrogasification gases produced in the hydrogasification reaction in the second catalyst bed, said hydrogasification gases containing substantially no vaporisable hydrocarbon capable of forming polymer.

3. A method as claimed in claim 1 or claim 2 wherein during stage (2) the second bed of catalyst and the first bed of catalyst are used in series.

4. A method as claimed in claim 3 wherein as the activity of the second bed of catalyst deteriorates the incompletely reacted reactants and the product gas are passed from the second bed to the regenerated first bed of catalyst where the steam reforming reaction is completed.

5. A method as claimed in claim 1 wherein the hydrogen containing gases used in the regeneration of the first catalyst bed are gasification gases produced by the steam reforming of vaporisable hydrocarbon feedstocks.

6. A method as claimed in claim 1 wherein the regeneration of the catalytic activity of the first bed of catalyst is effected by the passage through the said bed of hydrogasification gas, catalytic rich gas or a mixture thereof, under conditions whereby methane synthesis is effected.

7. A method as claimed in any one of the preceding claims wherein the catalyst used in the first and/or second bed is a co-precipitated nickel-alumina catalyst containing an addition of an oxide, hydroxide, or carbonate of an alkali metal or alkaline earth metal in a proportion of from 0.75 to 8.6% by weight calculated as metal based on the combined weight of nickel and alumina.

8. A method as claimed in claim 7 wherein the catalyst used in the first bed and/or second bed contains from 70 to 75% nickel and 0.8% potassium, the balance being alumina.

9. A method as claimed in any one of claims 1 to 6 wherein the catalyst used in the first bed and/or second bed is a co-precipitated nickel-alumina catalyst containing at least 40% nickel and from 0.10% to 0.75% of an alkali metal in the form of an alkali metal in the form of an oxide, hydroxide or carbonate, the percentages being

percentages by weight of metal based on the combined weight of nickel and alumina.

10. A method as claimed in claim 9 wherein the catalyst used in the first bed and/or second bed contains from 70 to 75% nickel and 0.2% potassium, the balance being alumina.
11. A method as claimed in any one of the preceding claims wherein the inlet temperature of the first bed and/or second bed of catalyst, when used in the steam reforming reaction, is in the range of from 350° to 450°C.
12. A method as claimed in any one of the preceding claims wherein the catalyst regeneration is effected at a temperature in the range of from 300°C to 550°C.
13. A method as claimed in any one of

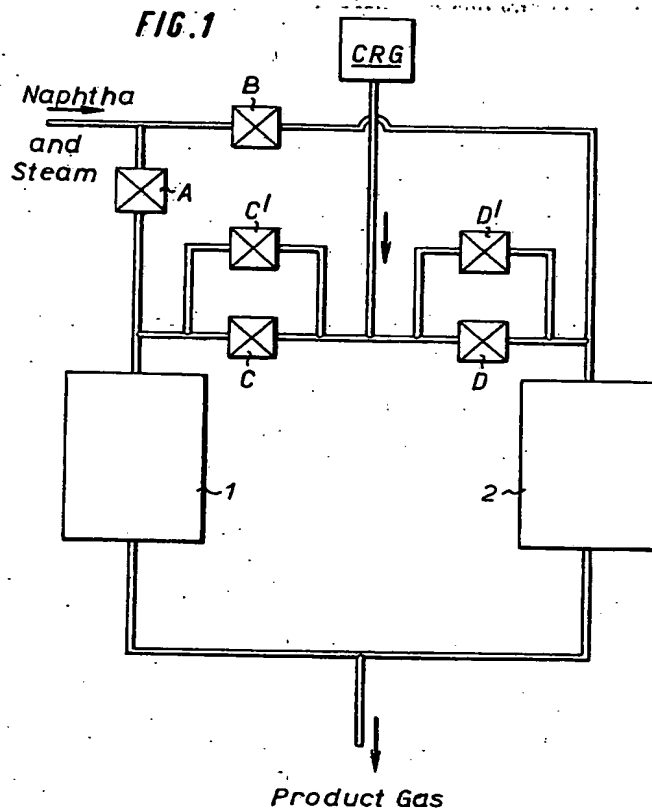
the preceding claims wherein the reforming reaction is carried out using the step of recycling a portion of the product gases produced in the reforming reaction and mixing these gases with the vaporisable hydrocarbon and steam to be reacted.

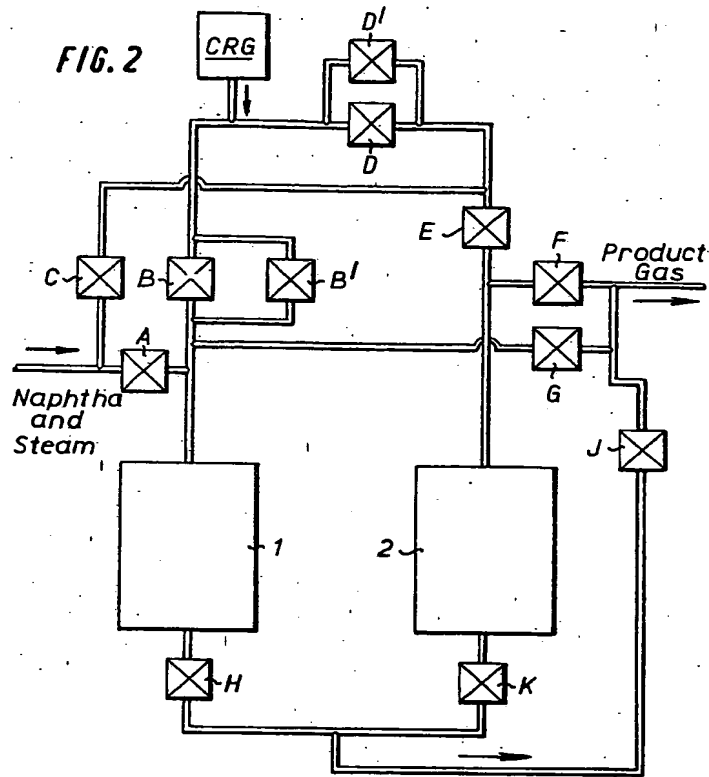
14. A method as claimed in claim 1 substantially as hereinbefore described with reference to Figures 1 to 3 of the accompanying drawings.

15. A method as claimed in claim 1 substantially as hereinbefore described with reference to Figure 4 of the accompanying drawings.

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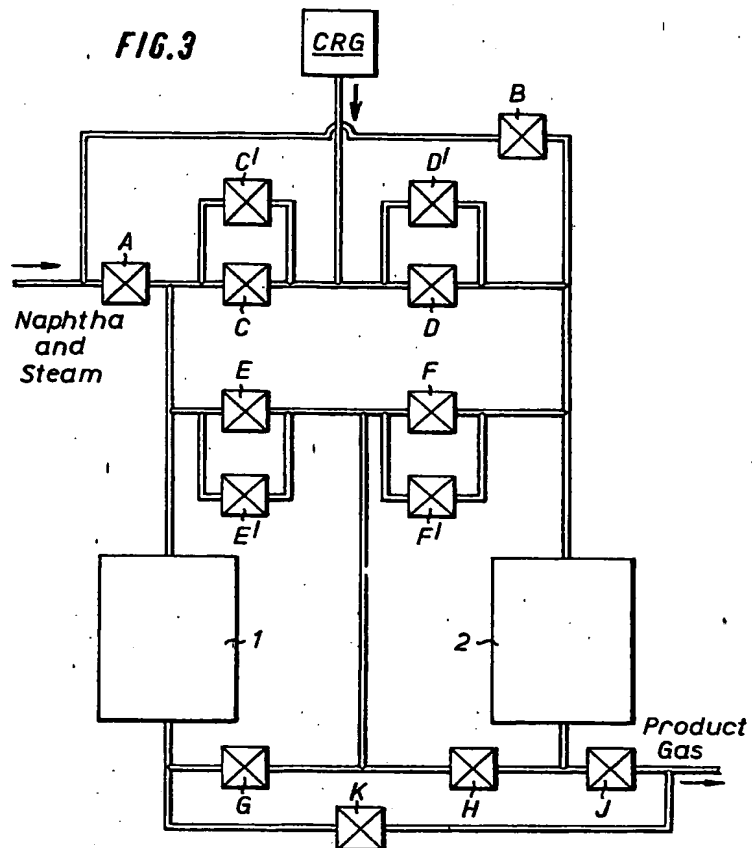


FIG. 4

